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(54) Title: WOOD IMPREGNATION

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mixture containing polymerizable organic compounds, and more particularly to a method for preparing a wood-polymer-composite
by impregnating wood material and/or wood-based material with a mixture containing polymerizable organic compounds, and most
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5   preparing a wood-polymer-composite by impregnating wood material and/or wood-based material with a mixture containing polymerizable organic compounds, and most particularly uses thereof.

BACKGROUND OF THE INVENTION

10   Wood-polymer composites of this category is based on polymerization of a monomer in the cavities of the cells (in-situ). The polymer produced is usually a thermoplastic (linear polymer). Monomers which belong to the vinyl monomer group are the ones usually used for this purpose. The vinyl monomers used are polymerized by means of radical chain

15   polymerization. The vinyl monomers are nonpolar, and will therefore not swell or react with the cell wall of the wood material. Some persons skilled in the art therefore claim that wood-polymer materials of this type are not "real" composites because there is no chemical bonding between the two combined materials. However, there is a high extent of

20   infiltration and the material acquires altered physical and mechanical properties, and hence should be defined as a novel type of material. Properties which are substantially increased are density, hardness, wear resistance and elastic modulus. Liquid water and water vapor movements in the new material are greatly reduced, especially along the

25   grain. In wood, transport along the grain is many times greater than across the grain, but in the new material they are about equal. Because the polymer does not react with the structure of the cell walls, the basic properties of the woody cell wall are not changed. Because the pores of the wood are blocked by polymer, the moisure can only move within the

30   unchanged woody cell wall, in spaces between the cell wall and the polymer in the lumen, or in any cracks that might be in the material. The time for humidification or drying of cell lumen wood-polymer composites will therefore be 10 to 20 times longer than for untreated wood. This

delay is an advantage in changing environments (especially a spill of liquid water). Because of the longer time, and because the polymer may induce a mechanical restraint of swelling, the dimensional stability of the new material is slightly improved. However, this can lead to local

5   stresses in the material, which can result in microcracks when the material is subjected to extreme moisture gradients.

The monomers usually utilized for cell lumen wood-polymer composite are methyl methacrylate and styrene and unsaturated polyester

10   oligomers, because of large supply of these chemicals and hence their low cost, as well as the relatively simple method of polymerizing them. Negative aspects of methyl methacrylate monomer are its subtantial shrinkage (up to 25%) during polymerization and relatively high vapor pressure (it evaporates easily). Negative aspects of styrene monomer

15   are its high vapor pressure (it evaporates easily) and easily-detectable odour (low odour threshold). A negative aspect of polyester oligomer is its higher viscosity which limits impregnation possibilities.

Monomer evaporation can lead to a low filling of surfaces by monomer.

20   Monomer shrinkage can lead to substantail shrinkage and warping of materials during cure, and can cause voids between polymer and cell wall. By selecting different types of monomers these problems may be reduced.

25   One problem of previously known wood-polymer composites of this category is that after impregnation and curing, they continue to liberate vinyl monomers which have an easily-detected odour and which can be irritating and injurious to health.

30   Other problems of previously known wood-polymer composites are cracking, warping and colour alteration of the materials. These indicate that temperatures of the curing phase caused by exothermic heat of reaction have been too high, resulting in excess shrinkage and pyrolysis

damage to the wood. The problem is increased dramatically with increased cross-sectional size, and in the past has limited the size of material which could be successfully treated.

5   Another problem of previously known wood-polymer composites results from a combination of moisture in the wood and the curing heat. Because of the exothermic heat of reaction, the temperature, especially of larger cross-sections, exceeds the boiling point of water. This causes rapid drying, followed by warping and cracking in moist wood. For this

10   reason, previous art successful treatment has been generally limited to dry (6% moisture content and less) wood.

SUMMARY OF THE INVENTION

It is the object of the invention to provide a polymer impregnated wood

15   of higher moisture content and having improved hardness, which also has low odour, and further, little cracking is observed in the finished material, thus eliminating the above disadvantages.

Essentially, this object is accomplished by using a wood material as a

20   starting material having a moisture content from about 3% to about 90%, in particular from about 15% to about 35%, especially from about 20% to about 30%, and preferably about 25%, and subjecting said starting material to specific polymerizable monomer formulations and impregnation and curing conditions.

25

The specific mixture of polymerizable monomers and additives combined with a specific curing temperature schedule is important for producing odourless materials.

30   When wood-polymer composites are manufactured, moisture may be a problem, because the reaction exotherm causes temperatures above the boiling point of water in larger cross sections regardless of the heating

method used. Rapid dehydration results. This causes deformations and cracks.

An essential feature of the present invention is to use starting wood materials having high moisture content. It is not prior knowledge to produce wood-polymer composites using moist wood as the starting material.

Wood, including cheap types and scrap material, can be used to produce noble wood materials such as imitation teak, mahogany, and others, and also provide them with novel properties like water resistance and simpler and reduced maintenance requirements. Since the monomers used are colourless, colours can be added, and thereby the finished product can be coloured throughout

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, the foregoing and other objects are attained by a product, method and uses thereof as disclosed in the patent claims.

An embodiment of this invention comprises a wood-polymer composite, characterized by wood impregnated with polymerizable monomers selected from a group consisting of styrene, methylstyrene and tertiary butylstyrene, initiated with at least three initiators; crosslinked with divinyl benzene, ethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, ethylene glycol trimethacrylate or trimethylol propane trimethacrylate and containing oil or wax as a polymerization moderator and water repellent for the finished product.

A second embodiment of this invention comprises a method for preparing a wood-polymer composite by impregnating wood material and/or wood-based material, characterized by the steps of:

utilizing said wood material having a moisture content of from about 15 to about 35% based on the weight of said wood material; impregnating said wood material with a composition selected from a group consisting of polymerizable monomers, a crosslinker and at least three initiators by means of vacuum and/or pressure; and curing said impregnated wood material in a hot air oven, steam or hot oil by means of a temperature sufficient to achieve the desired polymer loading.

A third embodiment of this invention comprises use of wood-polymer composite according to any of claims 1 to 9 or as manufactured according to any of claims 10 to 18, as a doorstep, doorlaminate, floor, handle, building board, pallet, acoustic wood, outdoor furniture, indoor furniture, container floor, play apparatus, benchtop, outdoor deck material, stair and railing material, fence stakes, or timber.

Particularly, said timber is a railway sleeper, especially an environmentally-friendly railway sleeper. Also, said timber can be a pole, especially an environmentally-friendly pole.

However, the use of said wood-polymer composite should not be restricted to those indicated above, but can include generally all kinds of use of wood products.

To obtain complete cure and low emissions from the finished product, it was found that a combination of initiators is needed. A lower temperature initiator starts the reaction, a second (higher temperature) carries it on and a third (highest temperature) finishes it. In most of these categories, alternative initiators may be used, depending on the reaction conditions, plant safety, cost and end-use requirements. Oil or wax is used to reduce the reaction exotherm during polymerization for the larger sizes of material, and also to act as water repellant for the material. The oil or wax has an additional benefit in that it is lower cost than monomer, reducing cost of the treatment.

The main monomers (styrene, methylstyrene (particularly para-methylstyrene) and tertiary butylstyrene) can be used alone or in any combination. The main advantage of methylstyrene and tertiary butylstyrene is their lower vapor pressure and thus lower emissions in

5   the production plant and the finished product.

Quantities of the initiators and crosslinkers used depend on product, process and end-use but are between a minimum and maximun value for each. Below the minimum value it will not work; above the maximum

10   value and the formulation will work but it is unnecessary and costly. Quantity of oil or wax is dependent on product size, curing conditions and desired end-use properties.

The mixtures used are shown in Table 1.

15

Table 1

Chemical	Second chemical (or alternate chemical)	Third chemical (or second alternate chemical)	Fourth chemical (or third alternate chemical)	Fifth chemical (or fourth alternate chemical)	Minimum % based on monomer	Maximum % based on monomer	Function
Styrene	Methylstyrene (vinyl toluene)	Tertiary butylstyrene					Main monomers
2,2'-Azobis(2-methylbutane-nitrile	Benzoyl peroxide	2,2'-Azobis(2,4-dimethyl-pentaneniitrile	2,2'-Azobis(2-methylpropanenit rile		0.1	0.3	Lower temperature initiator
1,1'-azobis(cyano-cyclohexane-carbonitrile)					0.1	0.3	Higher temperature initiator
Tertiary butyl perbenzoate	Di-tertiary butyl peroxide				0.5	1.5	Highest temperature initiator
Di-tertiary butyl peroxide					0.5	1.5	Highest temperature initiator (for high-temperature curing)
Divinyl benzene	Ethylene glycol dimethacrylate	Ethylene glycol tri-methacrylate	1,3-butylene glycol dimethacry-late	Trimethylol propane trimetha-crylate	2	5	Crosslinker
Petroleum oil	Vegetable oil	Petroleum wax	Vegetable wax		0	50	Additive

SUBSTITUTE SHEET (RULE 26)

The following examples will further illustrate the invention.

EXAMPLES

5   **BEECH TIMBERS**

       Materials and methods

       Six beech railway sleepers were used for the experiment. Some of these
       were cut into smaller samples and some were treated whole.

10   Type of wood: Beech (Fagus sylvatica)

       The dimensions of samples from the six beech sleepers were as follows:
       Small samples: 65 x 55 x 280 mm, 96 pieces;
       Medium samples: 55 x 145 x 800 mm; 12 pieces;
15   Large samples: 240 x 145 x 800 mm; 3 pieces;
       "Full scale": 240 x 145 x 1700 mm; 3 pieces.

       Table 2 shows the dry-density and moisture profile of the sleepers as
       used in the experiment. As seen in Table 2, the sleepers had high
20   moisture content. There was also great variation in moisture content
       among the sleepers and within each individual sleeper. Each of the six
       parts of Table 2 represent a cross section of an individual sleeper. It was
       expected that variations in moisture content also would be found in the
       longitudinal direction of each individual sleeper. Average dry-density of
25   the sleepers was 663 kg/m^3 ±39 kg/m^3.

Table 2 - Sample number (upper) dry-density in kg/m³ (center) and moisture content (lowest number) of the individual control samples taken from the cross section of the six sleepers

1 — 624 — 33,4%

1	3	5	7
611	626	629	586
27,7%	36,9%	36,1%	31,7%
2	4	6	8
630	621	661	628
30,0%	36,2%	37,9%	30,7%

2 — 662 — 30,2%

1	3	5	7
647	653	650	630
28,6%	32,3%	30,7%	27,9%
2	4	6	8
652	731	672	660
25,8%	33,7%	35,5%	27,2%

3 — 677 — 30,2%

1	3	5	7
714	697	687	659
30,5%	37,9%	37,1%	25,3%
2	4	6	8
664	666	659	673
23,7%	31,2%	29,3%	26,4%

4 — 671 — 27,3%

1	3	5	7
695	708	683	646
25,5%	34,6%	29,6%	22,3%
2	4	6	8
708	662	660	604
24,0%	30,4%	27,4%	24,5%

5 — 704 — 38,2%

1	3	5	7
699	679	664	645
38,5%	39,6%	33,1%	35,0%
2	4	6	8
806	717	721	702
41,0%	41,7%	43,1%	33,8%

6 — 640 — 28,1%

1	3	5	7
660	659	602	609
26,3%	27,4%	27,2%	27,5%
2	4	6	8
658	643	638	651
29,0%	30,7%	28,8%	27,6%

5

Impregnation

For all the treatments, "full-cell" impregnation was used. The wood product was placed in an autoclave and a vacuum of from about 0,01 to about 0,03 bar was established for a specific time (t_v) prior to filling the vessel with an impregnating fluid. When the fluid was in, atmospheric pressure was re-established and then an overpressure of about 7,5 bar was produced. The overpressure was maintained for a specific time (t_p).

Curing

All curing of monomer was carried out in a hot air oven having set temperatures of 70 and 140°C. Because the oven had residual heat in the heating elements, the temperature rose to 80°C after operation of several hours at a set temperature of 70°C. Nevertheless, the temperature of the curing is referred to as 70°C.

Completed treatments and evaluations thereof

Twenty-five different treatments were carried out. Each treatment was varied as regards the size of the wood materials, proportion of chemicals in the mixture, time of vacuum and pressure during the impregnating processes, as well as temperature and time of the curing processes. Four steps of the test were completed. A short description and evaluation of them is outlined hereinafter.

Step 1

Step 1 is comprised of sixteen different treatments of six small samples of each individual treatment. A sample from each sleeper was used such that variation of the wood materials of the different treatments were distributed as evenly as possible. These sixteen treatments were the basis for evaluation of impregnating quality, as well as evaluation of chemistry and curing completeness. Different times of vacuum and pressure were used. These are summarized in Table 3.

The treatments can be divided into four main groups; **a**: treatment 1-4, **b**: treatment 5-8, **c**: treatment 9-12, **d**: treatment 13-16.

Group a

Group a was treated using the first chemical formula. Time of vacuum was short, 5-8 min. Time of pressure was varied from 5 to 18 min. Time of curing at 70°C was varied from 3 to 6,5 h. Time of post-curing at 140°C was about 4 h. The conversion level of these treatments was low, thus indicating high evaporation of monomer during the curing process. Exothermic heat of reaction was not observed, indicating that the polymerization was not complete. No odour after completed curing was recognized, indicating very low values of residual monomer. As the samples dried, they shrank. The drying was severe, so it produced cracks in the materials. Residual moisture was estimated to be 0%.

Group b

After evaluation of group a, the concentration of initiator in the monomer mixture was increased. This was an attempt to initiate curing earlier. Time of vacuum was prolonged to 11-15 min. Time of pressure was

5　　varied from 4 to 19 min. Time of curing at 70°C was varied from 6 to 10 h. Time of post-curing at 140°C was 6 h. The samples were cooled before post-curing. During the longer curing time at 70°C, exothermic heat of reaction was detected. For treatments numbers 6, 7 and 8 this was observed after 7 h wherein the core temperature of the materials

10　　exceeded the surface temperature of the samples. No odour after completed post-curing at 140°C was recognized. Moisture reduction and crack formation were the same as observed for group a.

Group c

15　　After evaluation of group b, curing at 70°C without post-curing was done. The same chemical formula as for group b was used. Time of curing at 70°C was prolonged to 17-20 h to observe when the exothermic reaction occurred and how high the core temperature became. The core temperature exceeded the surface temperature after 5-7 h with a

20　　maximum occuring after 8,5-11 h. Time of vacuum was slightly reduced to 8,5-11 min. Time of pressure was varied from 4,5 to 28 min. Measuring was done after curing at 70°C. The odour was «medium» after curing at 70°C. This indicated residual monomers which have not reacted. To obtain consistent evaluation of polymer uptake, the samples

25　　were later post-cured at 140°C, but this is not reported in Table 3.

Group d

After evaluation of group c, it was decided to use another initiator in an attempt to start polymerization at an earlier stage and possibly increase

30　　conversion. For this group, measurements and evaluation were made after curing at 70°C. Post-curing at 140°C was carried out at a later stage to obtain consistent evaluation of polymer uptake and conversion. Time of vacuum was reduced to 5-12 min. Time of pressure was varied

from 0,5 to 4,5 min. Time of curing at 70°C was varied from 10 to 12 h. Dramatically shortening of the curing process was observed. The time until the core temperature exceeded the surface temperature was about 2 h, and the maximum temperature was observed according to 4,5 to 5 h. This effected the odour after treatment. The odour was classified as "low" which indicates a high level of conversion. Calculated conversion rose dramatically from 72% for groups a-c to 88% for group d. The new initiator was successful in reducing the reaction time and increasing conversion.

Step 2

Step 2 is comprised of three individual treatments of sleepers 1, 2 and 3. Details are given in Table 4, treatment numbers 17, 18 and 19.

Time of vacuum was varied from 11 to 14,5 min., and time of pressure was varied from 2,5 to 6,3 min. For the three treatments, temperature of the oven stabilized at 76 to 82°C. This was held for 18 h. The samples had a zone about 4 mm deep on the surface which had low polymer content, indicating monomer evaporation.

Half of all samples of step 2 were post-cured at 140°C for 20 h. This produced greater shrinkage, deformation and internal cracks in the materials. In addition, the core was dark brown as a result of the high temperature during such a long time. The internal cracks were not visible at the surface. The cracks had the same appearance as those produced by drying wood using conditions that are too severe. Post-curing resulted in a residual moisture of 0%. It is not possible to notice any odour from the materials and residual monomers were therefore considered to be at a very low level. This demonstrates the chemical mixture clearly affects the result.

Step 3

Step 3 was comprised of three individual treatments of large samples (full cross section) of sleeper 1, 2 and 3. Details are given in Table 4, treatments numbers 20, 21 and 22. Time of vacuum was varied from 5 to

5   7,5 min. For the three treatments, temperature of the oven stabilized at 84 to 88°C. This was held for 19-22 h.

Step 4

Step 4 was comprised of three individual treatments of "full scale"

10   samples of sleepers 4, 5 and 6. Details are given in Table 4, treatments numbers 23, 24 and 25. Time of vacuum was varied from 18 to 23 min. and time of pressure was varied from 8 to 9,5 min. For the three treatments, temperature of the oven stabilized at 86 to 88°C. This was held for 19-23 h.

15

Table 3 - Summary of treatments 1-16

Treatment No:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Samples	small	small	small	small	small	small	small	small	small	small	small	small	small	small	small	small
Number	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
Impregnating																
Wood	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech
Moisture	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.
Density	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.	measur.
Vacuum	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
Pressure	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
Time vacuum < 0, 1 bar (min.)	5,2	6,7	6,3	7,8	11,2	11,6	13,1	14,9	8,6	8,6	10,1	10,8	6,3	4,9	5,2	11,9
Time pressure > 7 bar (min.)	4,8	8,2	17,5	18,7	3,7	7,5	16,8	19,4	4,5	9,0	13,8	28,0	0,4	4,1	0,4	4,5
tot time process (min.)	26	29,9	37,3	41,0	28,0	32,8	44,0	48,5	28,0	31,7	37,7	54,1	19,4	24,3	23,9	31,3
Curing																
Heat source	oven	oven	oven	oven	oven	oven	oven	oven	oven	oven	oven	oven	oven	oven	oven	oven
Temperature 1	74	76	76	76	76	78	80	80	0	0	0	0	80	80	80	80
Temperature 2	136	140	140	140	136	140	140	140	82	82	82	82	0	0	0	0
Time temp I (h)	3	4,4	5,1	6,4	6	7,5	8,1	9,8	17	17,6	19	19,8	10	10,5	11,6	12,2
Time temp 2 (h)	4,2	4,2	4,2	4,2	6	6	6	6	0	0	0	0	0	0	0	0
Chemicals																
Vinyl-toluene	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%
Styrene	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%
Oil	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%
DVB (63%)	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%
1,1'-azobis (cyclohexane-carbonitrile)	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%	3,10%
DTBP (98%)	0,20%	0,20%	0,20%	0,20%	0,35%	0,35%	0,35%	0,35%	0,35%	0,35%	0,35%	0,35%	0,20%	0,20%	0,20%	0,20%
2,2'-azobis (2,4 dimethyl-pentanenitrile)	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,125%	0,125%	0,125%	0,125%
Measurements																
Moisture	25%	25%	25%	25%	24%	24%	24%	24%	20%	20%	20%	20%	16%	16%	16%	16%
weight (1) g	725	775	756	819	742	794	735	762	724	746	732	780	701	712	685	713
weight (2) g	1015	1083	1107	1157	1095	1129	1060	1096	1040	1061	1074	1115	1071	1073	1022	1066
weight (3) g					986	1013	934	967	926	937	938	968	996	1002	947	999
weight (4) g	787	858	862	882	852	869	828	846	850	870	862	876	928	938	888	924
Calculations																
Monomer loading	50,0%	49,7%	58,0%	51,6%	59,0%	52,3%	54,8%	54,4%	52,4%	50,7%	56,1%	51,5%	61,2%	58,8%	57,1%	57,4%
Polymer loading	35,7%	38,4%	42,5%	34,6%	42,4%	35,7%	39,7%	37,7%	40,9%	39,9%	41,3%	34,8%	53,6%	52,8%	50,4%	50,3%
Level of conversion	71,4%	77,3%	73,3%	67,1%	71,8%	68,3%	72,4%	69,3%	78,1 %	78,8%	73,7%	67,5%	87,5%	89,8%	88,3%	87,6%
Hardness 1	4,5	4,8	5,0	4,6	4,4	5,4	5,2	4,5	4,5	4,4	4,6	4,5	5,3	5,7	5,1	5,2
Hardness 2 (4 mm into sample)	4,2	6,3	7,4	7,0	5,7	7,0	6,8	7,1	8,7	7,3	5,6	7,5	10,0	8,9	9,7	9,6
Hardness control pr	3,3	3,4	3,1	3,3	3,1	3,5	3,1	3,1	3,3	3,4	3,1	3,3	3,1	3,5	3,1	3,1
Hardness improv.: % HB 1	36%	41 %	61 %	39%	42%	54%	68%	45%	36%	29%	48%	36%	71%	63%	65%	68%
Hardness improv.: % HB 2	27%	85%	139%	112%	84%	100%	119%	129%	164%	115%	81%	127%	223%	154%	213%	210%
Evaluation																
Odour	no odour	no odour	no odour	no odour	no odour	no odour	no odour	no odour	medium	medium	medium	medium	low	low	low	low
Colour	golden	golden	golden	golden	golden	golden	golden	golden	dry	dry	dry	dry	matt/dry	matt/dry	matt/dry	matt/dry

Table 4 - Summary of treatments 17-25

Treatment No:	Step 2			Step 3			Step 4		
	17	18	19	20	21	22	23	24	25
Samples	medium	medium	medium	full c.s.	full c.s.	full c.s.	full c.s.	full c.s.	full c.s.
Number	4	4	4						
Impregnating									
Type of wood	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech	Beech
Vacuum	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05	0,05
Pressure	7	7	7	7	7	7	7	7	7
Time vacuum < 0,1 bar	14,4	10,9	11,2	16,1	17,5	11,2	20,3	18,2	22,8
Time pressure > 7 bar	6,3	2,5	6,0	7,7	5,6	4,9	9,5	7,7	8,8
tot time process (min.)	36,4	25,2	28,4	34,0	34,7	26,6	39,6	35,7	42,0
Curing									
Heating source	oven	oven	oven	oven	oven	oven	oven	oven	oven
Temperature 1	77	76	82	88	88	84	86	86	88
Temperature 2	0	0	0	0	0	0	0	0	0
Time temp I (timer)	18	18	18	22	20	19	23	21	19
Time temp 2 (timer)	0	0	0	0	0	0	0	0	0
Chemicals									
Vinyl-toluene	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%	58,0%
Styrene	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%	25,5%
Oil	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%	16,5%
	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%	100,0%
DVB (63%)	3,10%	3,10%	3,10%	3.10%	3,10%	3,10%	3,10%	3,10%	3,10%
1,1'-azobis (cyclohexane-carbonitrile)	0,20%	0,20%	0,20%	0,20%	0,20%	0,20%	0,20%	0,20%	0,20%
DTBP (98%)	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%	0,30%
2,2'-azobis (2,4 dimethyl-pentanenitrile)	0,125%	0,125%	0,125%	0,125%	0,125%	0,125%	0,125%	0,125%	0,125%
Measurementsr									
Moisture	11,5%	15%	13%	28%	25%	25%	22%	33%	23%
weight (1) kg	3,81	4,4	4,33	20,2	21	21,2	43	46	39
weight (2) kg	5,88	6,3	6,07	30,5	30,5	28,5	57,5	58	58,5
weight (3) kg	5,47	5,78	5,72	28,6	28,4	26,3	54,5	55,5	56
Calculations									
Monomer loading	61,0%	50,0%	45,0%	65,0%	57,0%	43,0%	41,0%	35,0%	62,0%
Polymer loading	52,0%	40,0%	40,0%	57,0%	48,0%	34,0%	36,0%	31,0%	57,0%
Level of conversion	86,0%	79,0%	87,0%	87,0%	85,0%	79,0%	88,0%	91,0%	93,0%
Evaluation									
Odour	low	low	low	low	low	low	low	low	low
Colour	dry	dry	dry	dry	dry	dry	dry	dry	dry

Monomer and polymer loading and % conversion of monomer to polymer

Monomer and polymer loading, and conversion for the different treatments are given in Table 5, Table 6 and Table 7.

5

Table 5 - Monomer and polymer loading and conversion of monomer to polymer for the small samples

Treatment no.	Before imp. weight (g)	After imp. weight (g)	After curing weight (g)	Mc imp	*ML*	*PL*	*Conver.*
1	725	1015	787	18%	47%	28%	59%
	56	*43*	*32*	*6%*	*11%*	*4%*	
2	775	1083	858	21%	49%	34%	70%
	42	*50*	*42*	*8%*	*12%*	*10%*	
3	756	1107	863	25%	58%	42%	73%
	41	*34*	*49*	*9%*	*8%*	*10%*	
4	819	1157	882	31%	55%	42%	76%
	70	*14*	*50*	*5%*	*13%*	*14%*	
5	742	1095	852	23%	59%	41%	71%
	40	*33*	*59*	*6%*	*8%*	*13%*	
6	794	1129	869	29%	55%	41%	75%
	83	*15*	*37*	*11%*	*13%*	*10%*	
7	735	1060	828	24%	55%	40%	73%
	71	*65*	*40*	*8%*	*17%*	*11%*	
8	762	1096	846	24%	55%	38%	69%
	95	*41*	*32*	*9%*	*15%*	*9%*	
9	724	1040	850	18%	51%	38%	75%
	31	*37*	*37*	*3%*	*8%*	*7%*	
10	746	1061	870	16%	50%	36%	72 %
	61	*55*	*43*	*2%*	*15%*	*11%*	
11	732	1074	862	21%	57%	42%	75%
	34	*54*	*40*	*2%*	*13%*	*9%*	
12	780	1115	876	25%	54%	41%	75%
	39	*20*	*38*	*5%*	*9%*	*10%*	
13	701	1071	928	16%	62%	54%	88%
	36	*30*	*42*	*5%*	*9%*	*10%*	
14	713	1073	938	16%	59%	52%	89%
	53	*47*	*22*	*8%*	*9%*	*8%*	
15	685	1022	888	16%	57%	51%	88%
	45	*90*	*74*	*4%*	*20%*	*16%*	
16	713	1066	924	16%	58%	51%	88%
	74	*44*	*37*	*6%*	*14%*	*11%*	

Figures in italics are the standard deviation of the measurement of six samples of each treatment.
MC: "moisture content". Calculated average moisture content (dry basis) of the samples before
10 *impregnation.*
ML: "monomer loading". Calculated monomer uptake in % of dry-weight of the wood material.
PL: "polymer loading". Calculated polymer uptake in % of dry-weight of the wood material after curing at
140°C. It is expected that residual moisture is approximately 0 % after such a curing.
Conversion: % conversion of monomer to polymer.

Table 6 - Monomer and polymer loading and conversion of monomer to polymer for the medium-sized samples

Treatment no.	Sample no.	Weight before kg	Weight after kg	Weight cured 70°C	MC	ML	PL70°C (-3% mc)	Conv. 70°C
17	1B1	3,61	5,81	5,42	11%	68%	59%	87%
	1B2	3,91	6,04	5,60	12%	61%	52%	85%
	1B3	4,02	6,06	5,62	12%	57%	48%	84%
	1B4	3,68	5,59	5,24	11%	57%	50%	87%
	Average	**3,81**	**5,88**	**5,47**	**11%**	**61%**	**52%**	**86%**
18	2B1	4,52	6,28	5,67	14%	44%	32%	73%
	2B2	4,61	6,49	5,89	18%	48%	36%	75%
	2B3	4,48	6,38	5,87	16%	49%	39%	80%
	2B4	3,97	6,05	5,68	11%	58%	51%	88%
	Average	**4,40**	**6,30**	**5,78**	**15%**	**50%**	**40%**	**79%**
19	3B1	4,31	5,57	5,22	13%	33%	27%	82%
	3B2	4,53	6,44	6,03	14%	48%	41%	86%
	3B3	4,45	6,39	6,00	13%	49%	43%	87%
	3B4	4,02	5,89	5,61	10%	51%	47%	91%
	Average	**4,33**	**6,07**	**5,72**	**13%**	**45%**	**40%**	**87%**

No. of sample shows sleeper, section and location in the sleeper. Ex. 2B3 is a sample of sleeper no. 2, section B of board no. 3.
MC: "moisture content". Calculated average moisture content (dry basis) of the sample before impregnation.
ML: "monomer loading". Calculated monomer uptake in % of dry-weight of the wood material.
PL 70°C: "polymer loading". Calculated polymer uptake in % of dry-weight of the wood material. The samples were cured at 70°C.
The calculation assumes a 3 % moisture reduction during cure.
Conversion: % conversion of monomer to polymer.

Table 7 - Monomer and polymer loading and conversion of monomer to polymer for the large samples

Treat. no.	Length	Sample no.	Weight before kg	Weight after kg	Weight cured kg	MC	ML	PL70°C (3% mc)	Conv.
20		1c	20,2	30,5	28,6	28%	65%	57%	87%
21	80	2c	21,0	30,5	28,4	25%	57%	48%	85%
22	cm	3c	21,2	28,5	26,3	25%	43%	34%	79%
23		4c	43,0	57,5	54,5	22%	41%	36%	88%
24	170	5c	46,0	58,0	55,5	33%	35%	31%	91%
25	cm	6c	39,0	58,5	56,0	23%	62%	57%	93%

The three first samples had a length of about 80 cm and the three last samples had a length of about 170 cm. Sample number states sleeper and section. Ex. 4c, is a sample of sleeper no. 4, section C.
MC: "moisture content". Calculated average moisture content (dry basis) of the samples before impregnation.
ML: "monomer loading". Calculated monomer uptake in % of dry-weight of the wood material.
PL 70°C: "polymer loading". Calculated polymer uptake in % of dry-weight of the wood material. The samples were cured at 70°C.
The calculation assumes a 3 % moisture reduction during cure.
Conversion: % conversion of monomer to polymer.

Hardness of wood and the wood-polymer composite made from it is given in Table 8.

Table 8 - Changes in Brinell-scale (HB) hardness as a result of the treatments

Treatment no.	HB control	HB the surface	HB 4 mm	% increase HB surface	% increase HB – 4 mm
1	3,3	4,5	4,2	36%	26%
2	3,4	4,8	6,3	41%	85%
3	3,1	5,0	7,4	64%	141%
4	3,3	4,6	7,0	40%	115%
5	3,1	4,4	5,7	41%	80%
6	3,5	5,4	7,0	52%	97%
7	3,1	5,2	6,8	68%	119%
8	3,1	4,5	7,1	47%	133%
9	3,3	4,5	8,7	37%	162%
10	3,4	4,4	7,3	29%	115%
11	3,1	4,6	5,6	49%	81 %
12	3,3	4,5	7,5	38%	129%
13	3,1	5,3	10,0	67%	216%
14	3,5	5,7	8,9	62%	150%
15	3,1	5,1	9,7	65%	211%
16	3,1	5,2	9,6	70%	215%

PINE TIMBERS

Wood species: Scots pine (*Pinus sylvestris*)

Materials and methods

Ten sleepers were received and their moisture content (MC) and heartwood/sapwood location mapped for each sleeper. Each sleeper was weighed just before impregnation, after impregnation and after curing. MC was measured by cutting cores, separating them into increments, weighing each increment, ovendrying the increments and weighing them again. This method gave MC at various positions within each sleeper.

A 60 parts to 40 parts mixture of para-methyl styrene to styrene was the base monomer used. Based on the weight of this base monomer, the following ingredients were added: 20% mineral oil (reaction moderator and water repellant), 3,5% divinyl benzene (crosslinker), 0,5% 2,2'-azobis (2-methyl-butanenitrile) (low-temperature initiator), 0,2% 1,1'-azobis (cyclohexane-carbonitrile) (medium-temperature initiator) and 0,5% teriary butyl perbenzoate (high-temperature initiator).

Impregnation was carried out on all sleepers using vacuum for ½ hour, admitting monomer and then pressure of 5.3 bar. Pressure time for sleepers 1, 4 and 9 was ½ hour, for 2, 5, 6, 7 and 10 it was 1 hour and

5   for sleeper 8 pressure time was 3 hours.

Curing was carried out in a chamber 300 mm larger in all dimensions than a single sleeper. Temperature of the curing chamber, the surface of the sleeper and at locations within the sleeper was measured as curing

10   took place. Sleepers were treated and cured individually, except for the last two, which were processed together throughout.

Since rather severe internal checking ocurred in the sapwood portions of some of the first few sleepers treated, the curing temperature was

15   controlled in some subsequent sleepers to try to decrease this checking.

After curing, cross-sections were cut from each sleeper in locatoions where temperature had been measured, and polymer content assessed for the section. MC of the heartwood was also measured at that time

20   using cores. One sleeper was sawed longitudinally and densities were measured sequentially in sapwood, outer heartwood and inner heartwood for 1 m along the length.

Samples 50 mm square in cross section and 150 mm long were

25   prepared from untreated sapwood and heartwood, from treated heartwood, and from treated sapwood with and without internal checking. They were loaded perpendicular to the grain, parallel to the annual rings (tangentially), which is the same direction a rail plate would load them. The testing machine recorded load and displacement

30   (measured by LVDT) in a datalogger. The area was 50 mm by 50 mm, in the center of the sample.

Completed treatments and evaluations thereof

MC just before treating

Moisture contents determined at the time of treating are given in

5   Table 9.

Table 9 - Representative MC just before treatment

Sleeper #	Surface	Mid Sap	Deep Sap	Outer Heart	Inner Heart
1	27,7%	105,8%	122,7%	82,6%	30,3%
2	21,9%	30,6%	37,6%	28,8%	27,0%
3	18,5%	23,7%	25,6%	27,1%	25,1%
4	19,5%	33,5%	27,7%	26,2%	26,8%
5	24,8%	56,1%	33,0%	18,6%	28,8%
6	24,2%	33,6%	44,5%	32,6%	27,1%
7	20,8%	26,9%	28,1%	28,8%	29,1%
8	15,3%	16,3%	16,2%	24,2%	28,1%
9	19,4%	28,4%	26,7%	25,3%	27,6%
10	14,0%	16,6%	20,2%	23,5%	25,2%
Average	20,6%	37,2%	38,2%	31,8%	27,5%

10   Sapwood penetration by monomer of all sleepers except number 1 was

good because their MC was in the treatable range. Sapwood penetration

of sleeper number 1 was limited to the drier shell, with the wetter

sapwood not penetrated. Even so, overall uptake was similar to other

sleepers.

15

Curing quality

All sleepers cured and there was virtually no odour after cooling to room

temperature. Pre-existing surface checking expanded very little and no

new checks appeared.

20

Monomer in heartwood cured. This was determined by lack of smell and

hardness values equivalent to wood-polymer composites, and not the

lower values of untreated wood.

Internal checks in sapwood were minimized when curing temperature was moderated and when moisture content and sapwood depth were lower. The effect of curing temperature is shown in Table 10.

5   Table 10 - Maximum temperatures reached in sleeper, and effect on checking

Sleeper # (in sequence treated)	Surface	Shallow Sap	Deep Sap	Shallow Heart	Heart	Details	Checking
4	113,1	-	-	-	133,6		
9	107,2	119,5	-	-	98,5		
1	99,5	97,8	77,6	-	-	Sleeper mostly sapwood, limited penetration because of high MC	Little checking because of limited penetration
2	101,5	109,8	115,7	-	119,2		Considerable checking
7	111,4	115,3	125,1	-	98,6		Considerable checking
5	125,0	110,9	113,8	-	103,0		Considerable checking
8	99,6	99,6	98,1	-	87,5	Maximum temperature limited	Little checking
6	98,8	101,3	116,4	-	83,9	Cured with 10	Smaller and fewer checks
10	98,8	101,3	116,4	90,9	83,9	Maximum temperature limited, sleeper mostly heartwood	Smaller and fewer checks

Sleeper appearance was good and they were clean and able to be easily handled without skin protection.

10

Monomer and polymer loading

Table 11 summarizes the loading results.

Table 11 - Monomer and polymer loading of treated sleepers

Sleeper #	Unloaded (kg)	Monomer Loading (kg)	Polymer Loaded (kg)	Weight Loss (kg)	Loss
1	55,57	24,04	21,77	2,27	9,4%
2	39,35	20,86	19,16	1,70	8,2%
4	39,55	21,46	20,1	1,36	6,3%
5	38,56	16,44	14,85	1,59	9,7%
6	47,74	21,09	19,28	1,81	8,6%
7	45,93	15,53	15,08	0,45	2,9%
8	49,10	14,63	13,04	1,59	10,9%
9	37,78	16,65	14,38	2,27	13,6%
10	46,38	11	9,98	1,02	9,3%
	Average	17,97	16,40	1,56	8,8%

Average monomer loading of the nine sleepers was about 22 kg. The weight loss during cure was about 2 kg per sleeper or about 9% of the monomer weight. Since high temperatures, some above boiling point of water, were reached during cure, some of the weight loss must be water. Thus the 2 kg weight loss from a sleeper is partly water and partly monomer. If it were all monomer loss, another way to express would be that the monomer to polymer conversion was 91%, which is slightly higher than for the best beech sleeper treatment.

Loading of sapwood, heartwood and different locations and MCs
Polymer loading for different parts of the sleepers were calculated from density measurements made from pieces cut from them. Nearly all available space was filled by polymer in sapwood, giving densities just greater than 1 g/cc (average 1.03 g/cc). Heartwood loading was greatest near sleeper ends and around cracks, and decreased with distance from the sleeper end, becoming zero about 30 cm from the end. Polymer in heartwood was mostly in latewood and maximum loadings were near 50% of available space (average density of 0.72 g/cc).

Any sapwood below about 30% MC treated well and all heartwood MC was suitable for treating when the sleepers were received.

Quality

There were surface checks present before treatment. These enlarged slightly during treatment. Sapwood shrunk somewhat more than heartwood, producing some rounded (2 to 3 mm) surfaces. No warping occured. Sleeper appearance was good.

Compression strength and stiffness

The values of untreated and treated sleepers are reported in Table 12.

Table 12 - Stiffness and yield stress (MPa), density (g/cc) and polymer uptake of WPC and the untreated wood from which it was made

Treatment	Yield stress	MOE	Density	Uptake
Untreated pine heartwood	6	409	0,48	-
Untreated pine sapwood	5	991	0,54	-
Pine heartwood WPC	12	1058	0,74	51%
Pine sapwood WPC	50	3087	1,04	100%
Checked pine sapwood WPC	17	960	1,02	98%

Since stiffness (MOE) and yield stress (load at which the material begins to crush) are mostly determined by earlywood properties when loading is in the tangential direction, and since heartwood WPC polymer is found mostly in latewood, it is expected that heartwood WPC properties would be similar to untreated wood as is indicated in the table. The high loading of sapwood WPC (reflected in high densities) increased strength and stiffness greatly. Sapwood yield stress and MOE values are about the same as values for treated hardwoods like birch.

These results indicate that resistance to compressive loading and to mechanical wear should be noticeably better in WPC sleepers than in the wood from which it was made.

PATENT CLAIMS

1.   Wood-polymer composite, characterized by wood impregnated with polymerizable monomers selected from a group consisting of styrene, methylstyrene and tertiary butylstyrene, initiated with at least three initiators; crosslinked with divinyl benzene, ethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, ethylene glycol trimethacrylate or trimethylol propane trimethacrylate and containing oil or wax as a polymerization moderator and water repellent for the finished product.

2.   Wood-polymer composite according to claim 1, characterized in that said monomers are styrene, paramethyl styrene, tertiary butylstyrene and combinations thereof.

3.   Wood-polymer composite according to claim 1, characterized in that said initiators are selected in the following manner: at least one initiator is selected from a low temperature class initiator of 2,2'-azobis (2-methyl-butanenitrile), benzoyl peroxide, 2,2'-azobis (2,4-dimethyl-pentanenitrile), 2,2'-azobis (2-methyl-propanenitrile); at least one initiator is selected from a medium temperature class initiator of 1,1'-azobis (cyclohexane-carbonitrile) and 1,1'-azobis (cyanocyclohexane-carbonitrile); and at least one initiator is selected from a high temperature class initiator of tertiary butyl per-benzoate and di-tertiary butyl peroxide.

4.   Wood-polymer composite according to claim 1, characterized in that said polymerizable monomers presented as polymerized monomers are distributed throughout the whole of said composite, or within a shell below the exterior surfaces and ends 2 mm deep and deeper.

5.   Wood-polymer composite according to any of the preceding claims, characterized in that said composite containing said polymerized monomers has a density of from about 0,8 g/cc to about 1,2 g/cc.

6.   Wood-polymer composite according to any of the preceding claims,

characterized in that said composite untreated with said polymerizable monomers has an average moisture content from about 3 to about 90%, and the moisture content of said composite treated with said polymerizable monomers is from about 0 to about 50%.

7.   Wood-polymer composite according to any of the preceding claims,

characterized in that said composite is a round, sawn or laminated wood product.

8.   Wood-polymer composite according to claim 7,

characterized in that said wood product is a railway sleeper, especially an environmentally-friendly railway sleeper.

9.   Wood-polymer composite according to claim 7,

characterized in that said wood product is a pole, especially an environmentally-friendly pole.

10.   Method for preparing a wood-polymer composite by impregnating wood material and/or wood-based material,

characterized by the steps of:

utilizing said wood material having a moisture content of from about 15 to about 35% based on the weight of said wood material; impregnating said wood material with a composition selected from a group consisting of polymerizable monomers, a crosslinker and at least three initiators by means of vacuum and/or pressure; and curing said impregnated wood material in a hot air oven, steam or hot oil by means of a temperature sufficient to achieve the desired polymer loading.

11.   Method according to claim 10,

characterized in that said moisture content is about 25%.

12.   Method according to claim 10,

characterized in that said temperature of said hot air oven is from about 70 to about 140°C, preferably the temperature is about 70°C.

13.   Method according to claim 10,

characterized in that said polymerizable monomers are selected from the group consisting of styrene, methylstyrene and tertiary butylstyrene.

14.   Method according to claim 10,

characterized in that said crosslinker is divinyl benzene, ethylene glycol dimethacrylate, 1,3-butylene glycol dimethacrylate, ethylene glycol trimethacrylate, or trimethylol propane trimethacrylate.

15.   Method according to claim 10,

characterized in that impregnation is initiated with three initiators selected from low, medium and high temperature classes, wherein at least one initiator is selected from a low temperature class initiator of 2,2'-azobis (2-methyl-butanenitrile), benzoyl peroxide, 2,2'-azobis (2,4-dimethyl-pentanenitrile), 2,2'-azobis (2-methyl-propanenitrile), wherein at least one initiator is selected from a medium temperature class initiator of 1,1'-azobis (cyclohexane-carbonitrile) and 1,1'-azobis (cyanocyclohexane-carbonitrile), and wherein at least one initiator is selected from an initiator of high temperature class of tertiary butyl perbenzoate and di-tertiary butyl peroxide.

16.   Method according to claim 10,

characterized in that time of impregnation is from about 15 to about 45 minutes.

17.   Method according to claim 10,

characterized in that time of curing is from about 2 to about 12 h.

18.   Method according to claim 17,

characterized in that time of curing is about 8 h.

19.   Use of wood-polymer composite according to any of claims 1 to 9 or as manufactured according to any of claims 10 to 18, as a doorstep, doorlaminate, floor, handle, building board, pallet, acoustic wood, outdoor furniture, indoor furniture, container floor, play apparatus,

5   benchtop, outdoor deck material, stair and railing material, fence stakes, or timber.

20.   Use according to claim 19, wherein the timber is a railway sleeper, especially an environmentally-friendly railway sleeper.

21.   Use according to claim 20, wherein the timber is a

10   pole, especially an environmentally-friendly pole.